Thermodynamics of the Two-Phase Isochoric Heat Capacity in Compressible Fluids

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Thermodynamics of the isochoric heat capacity of fluids and binary fluid mixtures in the two-phase region has been considered. Special attention has been paid to the critical region and to the verification of the Yang-Yang equation, which relates the isochoric heat capacity to the second derivatives of chemical potential and pressure with respect to temperature. We have examined the behavior of these quantities in a theoretical crossover equation of state for a van der Waals fluid [1], and in the six-term crossover Landau model for real simple fluids and binary fluid mixtures of methane-ethane [2] and light-heavy water [3]. In pure fluids the behavior of the second derivative of the chemical potential with respect to temperature calculated along the saturation curve is affected by a non-trivial contribution associated with vapor-liquid asymmetry. It has been also shown that even small amount of impurities has a strong effect on the apparent near-critical behavior of the second derivative of chemical potential. Measuring the dependence of the isochoric heat capacity in the two-phase region on the overall density appears to be the most sensitive tool to detect small amounts of impurities in near-critical fluids. Available experimental data on the isochoric heat capacity of fluids in the two-phase region have been analyzed and possible effect of impurities has been discussed.

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